

Electron correlation and the phase diagram of Si

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Previous first-principles calculations of the melting properties of Si, based on the local-density approximation (LDA) for electronic exchange-correlation energy, under-predict the melting temperature by $\sim 20\%$. We present new first-principles results demonstrating that this problem is due to non-cancellation of exchange-correlation errors between the semiconducting solid and the metallic liquid. It is shown that other sources of error, particularly those due to system size and Brillouin-zone sampling, can be made negligible. The same LDA errors cause an underprediction of the pressure of the diamond-Si \rightarrow beta-tin-Si transition. The generalized-gradient approximation largely corrects both features of the Si phase diagram.

PACS numbers: 64.70.Dv 81.30.Dz 71.15.Pd

The long-standing ambition of calculating phase diagrams from first-principles quantum mechanics has become a reality in the last 10 years [1–4]. An important stimulus to the recent developments was the paper of Sugino and Car (hereafter SG) on the melting of Si [5]. The authors showed how the technique of thermodynamic integration [6] combined with first-principles molecular dynamics (FPMD) [7] based on density functional theory (DFT) can be used to calculate the free energy of solids and liquids, and hence melting curves, with no experimental input apart from fundamental constants. But although their paper was influential, their numerical results on Si were not very satisfactory, since their predicted melting temperature ($T_m = 1350$ K) was $\sim 20\%$ below the experimental value (1685 K) [8]. Our purpose here is to identify the cause of this discrepancy, which we shall argue comes from non-cancellation of DFT errors between the solid and liquid phases, and specifically from errors of the local-density approximation (LDA) used by SG. This has implications for the reliability of other first-principles work on phase diagrams.

The basic approximation in any DFT calculation is the algorithm adopted for exchange-correlation energy E_{xc} . Provided one can eliminate all other sources of error in calculating total energies and doing the statistical mechanics, then failure to reproduce experimental melting properties must be due to errors in E_{xc} . But it is often claimed, even by first-principles practitioners, that these other sources of error cannot be made small enough; in particular, it is claimed that first-principles calculations cannot yet be performed on large enough systems to render size errors negligible [4]. This was one of the major issues addressed by SG, who made strenuous efforts to ensure that their non- E_{xc} errors were negligible; the results presented later indicate that they were largely successful. Turning to E_{xc} errors, the crucial question is the extent to which they cancel between the coexisting phases. Since diamond-structure Si (d-Si) is a four-fold coordinated semiconductor and liquid Si (l-Si) is an approximately six-fold coordinated metal [9], electron screening

is likely to be very different in the two phases, so that non-cancellation of E_{xc} errors becomes an important issue. In considering this, we are helped by the fact that the pressure-stabilized β -tin structure (β -tin-Si) closely resembles the liquid in being metallic and six-fold coordinated. This suggests that there should be a close relation between the effect of E_{xc} errors on the melting temperature and on the d-Si \rightarrow β -tin-Si transition pressure, and an analysis of this relation will help us to confirm that errors in the LDA representation of E_{xc} account for the under-prediction of T_m .

Our first-principles calculations employ Vanderbilt ultra-soft pseudopotentials [10] and plane-wave basis sets. Most of our calculations are based on the local-density approximation (LDA) for E_{xc} used by SG, but we shall also present results using the generalized-gradient approximation (GGA) [11]. The calculations were done with the VASP code [12]. The plane-wave cut-off was 150 eV, which gives a convergence of 6 meV/atom in the difference of total (free) energies between liquid and solid, and the pseudopotential core radii were 1.31 Å. Our strategy for computing the free energies of solid and liquid differs somewhat from that of SG, and closely resembles that used in our recent work on Fe [1] and Al [3].

The Helmholtz free energy F of the solid can be written as $F = F_{\text{perf}} + F_{\text{vib}}$, where F_{perf} is the free energy of the perfect non-vibrating crystal (it is a *free* energy, because we allow for thermal electronic excitations), and F_{vib} is the contribution from lattice vibrations. The latter is written as $F_{\text{vib}} = F_{\text{harm}} + F_{\text{anharm}}$. The harmonic free energy per atom F_{harm} in the classical limit (melting occurs well above the Debye temperature) is: $F_{\text{harm}} = 3k_B T \ln(\hbar\bar{\omega}/k_B T)$, where the geometric-mean frequency $\bar{\omega}$ is given by:

$$\ln(\bar{\omega}) = N_{\mathbf{k}s}^{-1} \sum_{\mathbf{k}s} \ln(\omega_{\mathbf{k}s}), \quad (1)$$

with the sum going over wavevectors \mathbf{k} and branches s in the Brillouin zone, $N_{\mathbf{k}s}$ being the number of terms in the sum. The phonon frequencies $\omega_{\mathbf{k}s}$ are calculated using the small-displacement method. [13]

The anharmonic contribution F_{anharm} turns out to be very small (typically ~ 15 meV/atom near the melting temperature), so that it is accurately given by the second-order expansion:

$$F_{\text{anharm}} \simeq \langle U_{\text{anharm}} \rangle_{\text{harm}} - \langle U_{\text{anharm}}^2 \rangle_{\text{harm}} / 2k_{\text{B}}T, \quad (2)$$

where U_{anharm} is the anharmonic part of the first-principles total energy, and the thermal averages $\langle \cdot \rangle_{\text{harm}}$ are evaluated in the canonical ensemble of the first-principles harmonic system. We have verified the accuracy of Eq. (2) by comparing it with the exact expression: $F_{\text{anharm}} = -k_{\text{B}}T \ln \langle \exp(-U_{\text{anharm}}/k_{\text{B}}T) \rangle_{\text{harm}}$.

Our calculations of F_{perf} were performed on the primitive two-atom unit cell, at volumes from 16 to 22 Å³/atom with k -point sampling dense enough to give a precision of ~ 0.1 meV/atom. Results were fitted to the Birch-Murnaghan [14] form, which reproduces the data to within ~ 0.1 meV/atom. For F_{harm} , we calculated the force-constant matrix using 54-atom cells, with spot-checks on cells of up to 250 atoms indicating convergence to within ~ 2 meV/atom. The calculations were done at volumes from 18 to 21 Å³/atom, and $\ln(\bar{\omega})$ was fitted to a second-order polynomial $\ln(\bar{\omega}) = a + bV + cV^2$, which gives a fitting error in F_{harm} of ~ 1 meV/atom. The thermal averages needed to calculate F_{anharm} were done on a 54-atom cell at volumes of $V = 18$ and 20 Å³/atom and temperatures of 1000, 1500 and 2000 K. The results are accurately reproduced by the quadratic form $F_{\text{anharm}} = aT^2$, and to the accuracy we require it is enough to take the value $a = 7 \times 10^{-9}$ eV K⁻² for both volumes.

The free energy of the liquid is calculated using thermodynamic integration (TI), with the Stillinger-Weber [15] empirical total-energy model used as reference system. The difference of Helmholtz free energy $\Delta F \equiv F_{\text{AI}} - F_{\text{ref}}$ between the *ab initio* and Stillinger-Weber systems is obtained using the standard formula:

$$\Delta F = \int_0^1 d\lambda \langle U_{\text{AI}} - U_{\text{ref}} \rangle_{\lambda}, \quad (3)$$

with U_{AI} and U_{ref} the *ab initio* and reference total-energy functions, and $\langle \cdot \rangle_{\lambda}$ the thermal average evaluated in the ensemble of the system whose total-energy function is $U_{\lambda} \equiv (1 - \lambda)U_{\text{ref}} + \lambda U_{\text{AI}}$. In practice, the integral over λ is performed either by evaluating $\langle U - U_{\text{ref}} \rangle_{\lambda}$ at a set of λ values and using Simpson's rule, or by using 'adiabatic switching', in which λ is slowly and continuously varied between the two limits [16]. The reference free energy F_{ref} is calculated by thermodynamic integration starting from the Lennard-Jones system, for which accurate free energies have been published [17]. The calculation of F_{ref} is done on very large systems, so that it is converged with respect to system size to better than 1 meV/atom.

As has often been stressed [1], the final results for F_{AI} do not depend on the choice of reference system, but the

efficiency of the calculations can be greatly improved by careful tuning of the reference system, the criterion being that the strength of the fluctuations of $U_{\text{AI}} - U_{\text{ref}}$ should be made as small as possible. We find that in this sense the original parameters of the Stillinger-Weber model are far from optimal for liquid Si. Using *ab initio* MD simulations of l-Si at the state $V = 18.16$ Å³/atom, $T = 2000$ K, we have varied the Stillinger-Weber parameters to minimise the fluctuation strength, and it is the resulting 'optimized' SW model that we use as our reference model.

We made thorough tests of the convergence of ΔF with respect to system size and electronic k -point sampling by calculating it at the representative state point $V = 17$ Å³/atom and $T = 1750$ K, using systems of up to 512 atoms and up to 36 Monkhorst-Pack [18] k -points (results of these tests in Table 1). The tests were done as follows. The Γ -point results were obtained by explicit simulations on systems of all sizes, with ΔF calculated by thermodynamic integration (Eq. (3)). In most cases, we used the five λ values 0.0, 0.25, 0.5, 0.75 and 1.0 together with Simpson's rule, and comparisons with other sets of λ values show that the residual error from the integration itself is less than 5 meV/atom. We then used thermodynamic integration, with the Γ -point system as the reference system, to obtain the results for other k -point samplings. For systems of $N \geq 128$ atoms, the fluctuations of the difference of energies calculated with Γ -point and more k -points is small enough to allow the second-order expansion to be used instead of explicit TI, but for $N = 64$ this is not adequate and we used explicit TI.

The results of Table 1 show that with 64 atoms and four k -points the free-energy difference ΔF between *ab initio* and optimized Stillinger-Weber is converged to better than 10 meV/atom, and we have used this system to obtain F_{AI} for the liquid at the set of state points $V = 16, 17, 18, 19$ and 20 Å³/atom and $T = 1250, 1500$ and 1750 K. At each T , F_{AI} was fitted to a Birch-Murnaghan equation of state, the residual fitting error being no more than 2 meV/atom.

Our fitted *ab initio* Helmholtz free energies of d-Si and l-Si allow us to obtain the Gibbs free energy $G \equiv F - V(\partial F / \partial V)_T$, and hence the melting curve. The zero-pressure results for T_{m} and the entropy and volume of fusion, ΔS and ΔV , are compared in Table 2 with those of SG and the experimental values. Our very close agreement with the SG value of T_{m} (difference of only 50 K) confirms that their size and k -point errors were indeed very small, and also confirms that LDA under-predicts T_{m} by ~ 20 %. We note that our ΔS and ΔV values are both somewhat greater than those of SG.

We now turn to the matter of non-cancelling LDA errors between phases, exploiting the electronic and structural similarity between d-Si and β -tin-Si. At room temperature, the transition d-Si \rightarrow β -tin-Si occurs at an ex-

perimental pressure in the range 10.3 – 12.5 GPa [19] (although also a low value of 8.8 GPa has been reported [20]). Earlier LDA calculations on the static zero-temperature crystals gave transition pressures in the range 7.8–8.4 GPa [21,22], and our own calculations yield the value 7.8 GPa, which agrees closely with the earlier values. However, it has been shown that temperature has a strong influence on the transition pressure, which drops by $\sim 20\%$ as T goes from 0 K to room temperature [23], so that the temperature-corrected LDA pressure is too low by at least 4 GPa. It is also known that the generalized-gradient approximation (GGA) for E_{xc} significantly improves the predicted transition pressure. With the Perdew-Wang GGA [11], we find a transition pressure of 11.7 GPa (9.4 GPa when corrected to room temperature), which agrees closely with earlier GGA values [22]. Our calculations show that the main reason why LDA under-predicts the transition pressure is that it erroneously shifts the energy of d-Si upwards relative to β -tin-Si. The GGA goes a long way towards correcting this destabilization of d-Si. But a low melting temperature is also a sign of an erroneous destabilization of d-Si, and we hypothesize that the same underlying E_{xc} error is responsible for both under-predictions.

To test this hypothesis, we have recalculated the melting properties using GGA. It is instructive to do this by evaluating the free energy difference between the LDA and GGA systems. We have therefore performed long simulations for solid and liquid at the zero pressure volumes using the LDA, and calculated the GGA energies at a number of statistically independent configurations, for both the solid and the liquid. The calculations have been done on cells containing 64 atoms with four k -points, and spot-checked with calculations on cells containing 512 atoms and Γ -point sampling. Firstly, we found that the energy differences between GGA and LDA are basically constant, i.e. do not depend on the configurations of the atoms, which confirms the idea that the shift should be the same as for the low temperature static lattices. Secondly, we found that the free energy of the liquid is raised by 88 meV/atom relative to that of d-Si. Given an LDA entropy change on melting of $3.5k_{\text{B}}$ /atom, it is easy to work out a shift of melting temperature GGA-LDA of 292 K, bringing the GGA result to 1590 K, in much closer agreement with the experimental datum. We also found that, at the volumes corresponding to the LDA zero pressure, the GGA pressures are about 3.5 GPa larger than the LDA ones, so the GGA zero pressure volumes are larger. However, the bulk moduli for the solid and the liquid at the melting temperature are 78 and 34 GPa respectively, so the liquid will expand more than the solid in the GGA. We can estimate a new volume change on melting of 9.4%, which is also in somewhat better agreement with the experiments.

In summary, we have shown that the key issue in a first-principles account of the melting properties of Si is non-

cancellation of exchange-correlation errors between solid and liquid because of their different electronic structure. Technical errors due to system size and k -point sampling are readily brought under tight control. The basic reason why this can be done is that system size affects only the small difference of free energy between the first-principles system and a carefully designed reference system. The non-cancellation of exchange-correlation errors between coexisting semiconductor and metal is also responsible for difficulties in predicting the pressure of the diamond-Si \rightarrow β -tin-Si transition, and there is a quantitative relation between the error in this transition pressure and the error in melting temperature. The general implication is that for phase equilibria in which the coexisting phases have essentially the same electronic structure, e.g. the melting of high-pressure Fe, DFT calculations can be expected to predict phase equilibria with satisfactory accuracy.

ACKNOWLEDGMENTS

The work of DA is supported by a Royal Society University Research Fellowship. The calculations were performed at the UCL HiPerSPACE Centre, supported by HEFCE grant JR98UCGI and EPSRC grant GR/R38156. We acknowledge valuable discussions with R. Needs.

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N	ΔF_1	ΔF_4	ΔF_8	ΔF_{32}	ΔF_{36}
64	-4.165(5)	-4.262(5)	-4.253(5)	-4.257(5)	-4.257(5)
128	-4.282(5)	-4.250(5)			
216	-4.281(5)	-4.262(5)			
512	-4.248(5)	-4.251(5)			

TABLE I. Difference ΔF of Helmholtz free energy (in units of eV/atom) at thermodynamic state $V = 17 \text{ \AA}^3/\text{atom}$, $T = 1750 \text{ K}$, between the *ab-initio* and the Stillinger-Weber potential as function of size of simulated system (number of atoms N) and number of Monkhorst-Pack \mathbf{k} -points (subscript on ΔF).

	This work (LDA)	This work (GGA)	Sugino and Car [5]	Exper
$T_m(\text{K})$	1300(50)	1590(50)	1350(100)	1685
$\Delta V_m/V_s$	0.142	0.094	0.1	0.119 ^b
ΔS_m	3.5		3.0	3.6 ^d
dT_m/dP	-58		-50	-3

^a Ref. [8]

^b Ref. [24]

^c Ref. [25]

^d Ref. [26]

TABLE II. Comparison of calculated and experimental melting properties of Si at ambient pressure: melting temperature T_m , volume change ΔV_m divided by volume of solid at melting temperature, entropy change ΔS_m per atom divided by Boltzmann's constant, and slope of melting curve dT_m/dP (units of K GPa⁻¹).